

PTO 06-7206

CY=JA DATE=19910701 KIND=A  
PN=03-153523

LAMINAR ACTIVE ALUMINA CARRIER, PRODUCTION METHOD THEREOF,  
AND COMPOSITE PIGMENT THAT EMPLOYS IT  
[Hakuhenjo Kassei Arumina Tantai, Sono Seizo Hoho,  
Oyobi Sorewo Mochiita Fukugo Ganryo]

Masanobu Wakasa, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. October 2006

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	03153523
DOCUMENT KIND	(12):	A
	(13):	PUBLISHED UNEXAMINED APPLICATION (Kokai)
PUBLICATION DATE	(43):	19910701
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	01294388
APPLICATION DATE	(22):	19891113
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	C01F 7/42
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTORS	(72):	WAKASA, MASANOBU; SAKAGUCHI, MIKIO
APPLICANT	(71):	KAO CORPORATION
TITLE	(54):	LAMINAR ACTIVE ALUMINA CARRIER, PRODUCTION METHOD THEREOF, AND COMPOSITE PIGMENT THAT EMPLOYS IT
FOREIGN TITLE	[54A]:	Hakuhenjo Kassei Arumina Tantai, Sono Seizo Hoho, Oyobi Sorewo Mochiita Fukugo Ganryo

## 1. Title

LAMINAR ACTIVE ALUMINA CARRIER, PRODUCTION METHOD THEREOF, AND  
COMPOSITE PIGMENT THAT EMPLOYS IT

## 2. Claims

1. A laminar active alumina carrier having an average particle size of from 0.1 to 50  $\mu\text{m}$ , an aspect ratio of from 10 to 100, and a specific surface area of from 30 to 350  $\text{m}^2/\text{g}$ .

2. The laminar active alumina carrier recited in Claim 1 that has a pH of from 3.0 to 5.0 when it is formed into a suspension.

3. A method for producing the laminar active alumina carrier recited in Claim 1 comprising treating laminar metallic aluminum that has an average particle size of from 0.1 to 50  $\mu\text{m}$ , an aspect ratio of from 10 to 100, and a specific surface area of from 2 to 20  $\text{m}^2/\text{g}$  with an alkali at a pH of from 7.1 to 11.0 and subsequently drying and/or firing it.

4. The method for producing the laminar active alumina carrier recited in Claim 2 comprising further treating the laminar active alumina carrier obtained by the method recited in Claim 3 with an acid and subsequently drying and/or firing it.

5. A composite pigment that is comprised of the laminar active alumina carrier recited in Claim 1 or 2 within which is held an

---

\* Number in the margin indicates pagination in the foreign text.

organic pigment and whose surface is subjected to a hydrothermal treatment.

### 3. Detailed Description of the Invention

#### [Field of Industrial Application]

The present invention pertains to a novel active alumina carrier. More specifically, it pertains to a laminar active alumina carrier that has a high pigment adsorptive property, rendering it highly useful as a pigment carrier, to a production method thereof, and to pigments that are prepared by causing said laminar active alumina carrier to hold organic pigments within it and that have high brightness, chroma saturation, water resistance, solvent resistance, weather resistance, and safety as well as excellent extensibility (spreadability, smoothness), thus having excellent sensory performance.

#### [Prior Art and Problems that the Invention Intends to Solve]

Organic pigments are superior to inorganic pigments in vividness of their colors and an abundance of variety, but many of them are inferior in their stabilities, such as water resistance, solvent resistance, weather resistance, heat resistance, etc. On the other hand, many inorganic pigments are excellent with respect to these /126 stabilities, but they have problems in that their colors are typically dull, that the variety of colors is also limited, and so forth. Accordingly, attempts have been made to create composites for the purpose of obtaining pigments having the excellent properties of both organic and inorganic pigments.

For example, there is known a method that coats the surface of an inorganic powder of titanium oxide, barium sulfate, etc., with an organic pigment and insolubilizes it to improve opacifying power and weather resistance and a method that causes a clay mineral, shirasu balloon, or other active inorganic powder to hold an organic pigment within it by means of ion exchange, adsorption, or the like, thereby obtaining a pigment.

However, with respect to the method that coats an inorganic powder with an organic powder, the coated organic pigment separates easily, and, since the organic pigment is exposed at the surface, the improvement of water resistance, solvent resistance, weather resistance, etc., is naturally limited; consequently, this method has had the problem of not being able to ameliorate the shortcomings of organic pigments sufficiently. The method that causes an inorganic pigment to hold an organic pigment within it has problems in that the vividness of the organic pigment is often sacrificed and that, if the organic pigment is not sealed in completely, water resistance, solvent resistance, and weather resistance deteriorate.

Accordingly, the present inventors researched extensively to overcome these technical challenges and found ~~porous alumina~~ that has excellent pigment adsorptive power, that does not affect the color tone of said adsorbed pigment at all, and that has properties required of a stable pigment carrier. Based on this finding, they applied for a patent (see JP S60-20555.) Although this alumina provided excellent

stability and vivid color tone when used in pigments, organoleptic tests that were recently conducted on its sensory performance in use as cosmetic products revealed that it was not satisfactory in extensibility factors, such as spreadability, smoothness, etc., and there was a limit to its concentration when used in cosmetic products.

Conventionally, alumina is produced by dehydrating aluminum hydroxide (or alumina hydrate) that is obtained by (1) neutralizing an aqueous solution of an aluminum salt with ammonia or alkali, (2) by precipitating it from a supersaturated solution of sodium aluminate or by hydrolyzing sodium aluminate with carbon dioxide, sodium hydrogen carbonate, or an acid, (3) by hydrolyzing an aluminum amalgam, (4) by hydrolyzing an alkylated product or alkoxide of aluminum, or the like.

Conventional alumina obtained by these methods, however, was produced only in fine powder form, spherical form, or granular form and, consequently, had insufficient extensibility, which gave rise to a problem in sensory performance in use.

Meanwhile, in Japanese Patent Laid-Open Publication No. Sho. 51-100995 is disclosed a method that reacts metallic aluminum in an alkaline, neutral, or acidic aqueous solution to obtain aluminum hydrate in fine powder form, in plate shape, or in gel form, respectively. The aluminas obtained by this method, however, all have a specific surface area of  $30 \text{ m}^2/\text{g}$  or less and, consequently, have poor performance as a carrier, and they also have extremely small particle sizes and, as a result, have poor extensibility, thus giving

rise to the problem of poor organoleptic attributes, such as a grating feeling, etc.

Accordingly, there has been a need for the development of a novel active alumina carrier that has excellent characteristics as a carrier of pigments and that yields excellent sensory performance when used in cosmetic products.

[Means for Solving the Problems]

In this situation, the present inventors conducted extensive research and, as a result, learned that a laminar active alumina carrier that is highly active can be obtained by treating laminar metallic aluminum having a certain average particle size, aspect ratio, and specific surface area with an alkali and subsequently by drying and/or firing it and also learned that a process of causing said carrier to hold an inorganic pigment within it and subsequently subjecting it to a hydrothermal treatment yields a composite pigment that has excellent organoleptic attributes and that also has substantially improved water resistance and solvent resistance. Based on these findings, the present invention was achieved.

That is, the present invention provides a laminar active alumina carrier having an average particle size of from 0.1 to 50  $\mu\text{m}$ , an aspect ratio of from 10 to 100, and a specific surface area of from 30 to 350  $\text{m}^2/\text{g}$ , a production method thereof, and composite pigments that utilize said carrier.

In the present invention, average particle size is a value that was found by dispersing a powder suspension with ultrasound and then by measuring its particle size using a laser diffraction particle size distribution analyzer. Aspect ratio is a value obtained by measuring, using an electron scanning microscope, the maximum diameter and maximum thickness of a group of particles in one field of view, from which the ratio of the diameter and thickness was calculated, and subsequently by averaging the ratios obtained from twenty fields of view. Specific surface area is a value obtained by the BET method /127 with N<sub>2</sub> adsorption. The pH of a suspension is a value that was obtained by measuring the pH of a 5 % by weight aqueous suspension at 25 °C.

The term "laminar" in the present invention means any shape that is thinner in the direction of thickness compared with the direction of width, including platy, leafy, discoidal, scaly, flaky, etc., shapes.

The term "active alumina" in the present invention means alumina that not only has a large specific surface area but also can partially, at the least, be converted into hydrated alumina, and it includes amorphous,  $\chi$ -,  $\rho$ -, and  $\eta$ -aluminas, boehmite, and the like. It also includes aluminas obtained by forming solid acid sites on the surface of the aforesaid aluminas to improve their adsorptive property.

The average particle size of the laminar active alumina carrier must be in the range of from 0.1 to 50  $\mu\text{m}$ , preferably from 1 to 20  $\mu\text{m}$ .



If its average particle size exceeds 50  $\mu\text{m}$ , it lacks adhesion (adherence) to the skin when it is used in a cosmetic product, and an average particle size that is smaller than 0.1  $\mu\text{m}$  causes extensibility to deteriorate.

The laminar active alumina carrier of the present invention must be in a laminar shape whose aspect ratio is in a range of from 10 to 100. If the aspect ratio is smaller than 10, the resulting pigment does not exhibit good extensibility. As the aspect ratio increases, the extensibility of the resulting pigment improves, but it is technically difficult to achieve an aspect ratio of 100 or higher.

Its specific surface area must be in a range of from 30 to 350  $\text{m}^2/\text{g}$ , preferably from 200 to 350  $\text{m}^2/\text{g}$ , so as to be able to adsorb organic pigments well. If the specific surface area is less than 30  $\text{m}^2/\text{g}$ , the adsorption of organic pigments becomes insufficient, while it is technically difficult to prepare a carrier having a specific surface area exceeding 350  $\text{m}^2/\text{g}$ .

The laminar active alumina carrier of the present invention is capable of adsorbing organic pigments even without having solid acid sites, but a carrier having solid acid sites whose suspension has a pH of from 3.0 to 5.0 exhibits higher adsorption of organic pigments.

Such a laminar active alumina carrier of the present invention can be produced by treating laminar metallic aluminum having a specific surface area of from 2  $\text{m}^2/\text{g}$  to 20  $\text{m}^2/\text{g}$ , an aspect ratio of from 10 to 100, and an average particle size of from 0.1 to 50  $\mu\text{m}$  with

an alkali at from pH 7.1 to pH 11.0 and subsequently by drying and/or firing it, or it can be produced by further treating the laminar active alumina carrier obtained by the aforesaid method with an acid and subsequently by drying and/or firing it.

The production method of the present invention can yield a laminar active alumina carrier that mostly retains the shape of the laminar metallic aluminum used as the raw material; as a result, by controlling the shape of the raw material metallic aluminum, the shape of resulting laminar active alumina carrier can be easily controlled.

The present invention can use, as the starting material, laminar metallic aluminum that is obtained by pulverizing atomized aluminum powder or aluminum chips together with a lubricating agent, such as stearic acid, etc., and mineral spirits with a ball mill until a given particle size is achieved and by subsequently classifying the product with a wet-type vibration sieve, which is followed by filtration.

The laminar metallic aluminum thus obtained is stirred in an alkali aqueous solution to treat it. The alkali used here includes hydroxides of alkali metals and alkaline earth metals, alkali metal carbonates, ammonia, amines, and urea, among which ammonia, urea, and amines, such as monoethanol amine, etc., are preferable. The pH of the alkali aqueous solution must be in a range of from 7.1 to 11.0, preferably from 9.0 to 10.0, in order to inhibit a rapid reaction. The reaction temperature is preferably in a range of from 40 to 100 °C, better yet, from 70 to 90 °C, in order to inhibit a rapid reaction.

Furthermore, adding a surface active agent in the alkali treatment reaction for the purpose of preventing the agglomeration of the laminar active alumina carrier yields a desirable result. The surface active agent added here is preferably an anionic surface active agent, better yet, a polymeric surface active agent of the polycarboxylic acid type.

After the alkali treatment is thus carried out, the product is filtered and dried. Performing a firing process on this product can further improve its pigment adsorptive power. The firing temperature is preferably in a range of from 150 to 800 °C, and, when the firing is conducted at a temperature of from 400 to 600 °C for from 10 minutes to 2 hours, a laminar active alumina carrier having the most excellent characteristics can be obtained. /128

To obtain a laminar active alumina carrier of the present invention having solid acid sites whose suspension has a pH of 3.0 to 5.0, a suspension of the laminar active alumina obtained in the foregoing is treated with a mineral acid, such as hydrochloric acid, sulfuric acid, nitric acid, etc., or an organic acid, such as oxalic acid, citric acid, etc., and subsequently dried and/or fired.

The acid treatment with these organic acids is preferably conducted under a condition that sets the pH of the suspension in equilibrium to from 2 to 5.5. If the pH is less than 2, alumina is dissolved, which could cause the carrier particles to dissolve, and a pH exceeding 5.5 is not desirable because the subsequent activation

becomes difficult, thus adversely affecting the pigment adsorptive power.

By firing the product that is obtained by filtering and drying after such an acid treatment, a laminar active alumina carrier having further improved pigment adsorptive power can be obtained. Here, the firing temperature is preferably in a range of from 150 to 800 °C, and it is particularly desirable to perform the firing at a temperature of from 350 to 600 °C for 10 minutes to 2 hours.

By causing the laminar active alumina of the present invention thus obtained to adsorb an organic pigment and hold it within, a composite pigment that has a vivid color and that is stable can be obtained.

Examples of the organic pigment that is held inside the laminar active alumina carrier include acid dyes, natural colorants, oil-soluble dyes, vat dyes, and so forth, and any of these may be used to impart a color, but it is particularly preferable to use acid dyes and natural colorants.

Examples of acid dyes include Red No. 2, Red No. 3, Red No. 102, Red No. 104, Red No. 105, Red No. 106, Yellow No. 4, Yellow No. 5, Green No. 3, Blue No. 1, Blue No. 2, Red No. 227, Red No. 230, Red No. 231, Red No. 232, Orange No. 205, Orange No. 207, Yellow No. 202, Yellow No. 203, Green No. 201, Green No. 204, Green No. 205, Red No. 202, Blue No. 205, Brown No. 201, Red No. 410, Red No. 502, Red No. 503, Red No. 504, Red No. 506, Orange No. 402, Yellow No. 402, Yellow

No. 403, Yellow No. 406, Yellow No. 407, Green No. 402, Purple No. 401, Black No. 401, and so forth, and, as necessary, these may be used as mixtures.

Natural colorants include quinone pigments, such as laccaic acid, carminic acid, kermesic acid, alizarin, shikonin, alkanine, equinochrome, etc.; carotenoid pigments, such as  $\beta$ -carotin,  $\beta$ -apo-8-carotenal, capsanthin, lycopene, bixin, crocin, canthaxanthin, etc.; flavonoid pigments, such as shisonin, raphanin, oenocyanine, safole yellow, rutin, quercetin, cacao pigment, etc.; flavine pigments, such as riboflavin, etc.; porphyrin pigments, such as chlorophyll, etc.; diketone pigments, such as curcumin, etc.; betacyanidin pigments, such as betanin, etc.; and so forth, and these may be used as mixtures, as necessary.

Examples of oil-soluble dyes include Red No. 215, Red No. 218, Red No. 223, Orange No. 201, Orange No. 206, Yellow No. 201, Yellow No. 204, Green No. 202, Purple No. 201, Red No. 501, Red No. 505, Orange No. 403, Yellow No. 404, Yellow No. 405, Blue No. 403, etc., and these may be used as mixtures, as necessary.

The adsorption process is carried out by brining a 0.001 to 10 % by weight, preferably 0.01 to 3 % by weight, solution of the aforesaid organic pigments into contact with, and reacting it with, the laminar active alumina carrier prepared in the aforesaid manner.

AS for the pigment solution, an aqueous solution is desirable for acid dyes or natural colorants, and an organic solvent solution is

preferable for oil-soluble dyes, but, depending on the case, a mixture solution of water and an organic solvent can be used. In the case of producing a vat dye, an aqueous solution of a reductant is employed.

The pigment solution may incorporate surface active agents, inorganic salts, etc., for the purpose of improve dyeing affinity, if necessary.

The operation of contacting and reacting the laminar active alumina carrier and the pigment solution can be carried out by such a method as immersion, drop addition, or fluid bed mixing, but, with any method, it is preferable to set the contacting and reaction time to from 1 to 60 minutes and to set the temperature of the pigment solution to 80 °C or lower. When an organic pigment is held inside the carrier by this contacting and reaction operation at a weight ratio of from 0.001 to 1 g per 1 g of the carrier, preferably from 0.05 to 0.8 g per 1 g of the carrier, the resulting pigment has desirable /129 characteristics.

The active alumina carrier that holds an organic pigment inside it can be partially formed into a hydrate by further treating it hydrothermally. This hydrothermal reaction can prevent the organic pigment from dissolving out.

A treatment with hot water at a temperature of from 70 to 180 °C is sufficient as the hydrothermal treatment, but the use of pressurized steam at a temperature of 100 to 180 °C is especially preferable because this further improves the effect of the

hydrothermal treatment. However, since some organic pigments are discolored at a temperature exceeding 150 °C, care must be taken. With respect to the time required for the hydrothermal treatment, the higher the temperature, the shorter the time required, and, therefore, the time should be determined according to the temperature, but it is preferably from 5 minutes to 2 hours.

After the hydrothermal treatment, the powder, at the final stage, is washed, filtered, and dried at a temperature of 120 °C or lower. In this process, washing with an organic solvent, such as acetone, ethanol, etc., for the purpose of accelerating the drying of the filtered product and of preventing secondary agglomeration yields a product having excellent powder properties.

The composite pigment of the present invention obtained in this manner has excellent color tone, dyeing power, sensory performance, water resistance, solvent resistance, and safety, and cosmetic products into which it is blended have both vivid external color with no color separation and excellent sensory performance in use.

Furthermore, coating materials into which it is blended have vivid external color as well as weather resistance, water resistance, and solvent resistance.

#### [Operation]

The alumina carrier of the present invention is laminar, has a large specific surface area, thus being highly active, and can also be hydrated by a hydrothermal treatment. As a result, it has a high

pigment adsorptive property and is capable of preventing a pigment from dissolving out, thereby making it possible to obtain pigments that have excellent color tone, water resistance, solvent resistance, weather resistance, and safety, and that have excellent sensory performance owing to their good extensibility.

#### [Effects of the Invention]

Because the laminar active alumina carrier of the present invention has excellent sensory performance as well as excellent adsorptive characteristics owing to its large specific surface area, it is useful as an extender that has various functions, such as the function of holding moisture-absorbing components, oil-absorbing components, aroma-retaining components, and medicinal components.

Such a composite pigment prepared by using the laminar active alumina carrier of the present invention does not show color separation in use and has a highly vivid external color, excellent water resistance, and oil resistance, rendering it useful for various cosmetic products, coating materials, plastics, inks, artists' colors, everyday sundries, decorative products, etc.

#### [Working Examples]

The following explains the present invention by presenting some working examples.

##### Reference Example 1

An atomized powder of metallic aluminum, together with stearic acid and mineral spirits, was pulverized with a ball mill to a given



particle size, and the product was subsequently classified with a wet-type vibration sieve and filtered, thereby obtaining laminar metallic aluminum having a specific surface area of 4 m<sup>2</sup>/g, an aspect ratio of 70, and an average particle size of 19.0 μm.

#### Working Example 1

To a solution comprised of 200 g of 0.1 % aqueous ammonia and 160 g ethanol was added 10.0 g of the aforesaid laminar metallic aluminum. The pH of the suspension at this stage was 10.0. The suspension was stirred for 1 hour at 80 °C, thereby fully completing the reaction. After suction filtration, drying was conducted at 90 °C for 2 hours, thereby obtaining 16.3 g of a white powder. Next, the powder was fired at 400 °C for 2 hours in a nitrogen ambience, thereby obtaining 11.5 g of a laminar powder having a specific surface area of 268 m<sup>2</sup>/g, an aspect ratio of 50, and an average particle size of 20.0 μm.

#### Working Example 2

To a solution comprised of 160 g ethanol and 200 g water was added 10.0 g of the same laminar metallic aluminum obtained in Working Example 1. To this was then added 0.1 g of a specialty polymeric surface active agent of the polycarboxylic acid type (Demol BP, a product of Kao Corporation), and the mixture was stirred for 30 minutes. Thereafter, 0.9 g monoethanol amine was added. The pH of the mixture at 25 °C at this stage was 10.0. The mixture was stirred for 2 hours at 80 °C, thereby fully completing the reaction. After suction filtration, drying was conducted at 90 °C for 2 hours, thereby

obtaining 16.5 g of a white powder (laminar powder A). The powder was further fired at 400 °C for 2 hours in a nitrogen ambience, thereby obtaining 11.8 g of a laminar powder having a specific surface area of 278 m<sup>2</sup>/g, an aspect ratio of 50, and an average particle size of 20.0 μm (laminar powder B).

#### Working Example 3

To 10.0 g of powder A obtained in Working Example 2 was added /130 170 g water, and the mixture was stirred. The pH of this suspension at this stage as measured at 25 °C was 7.1. After 4 mL of 1N hydrochloric acid was added to the suspension, thereby adjusting its pH to 3.60, the suspension was stirred for 2 hours. An equilibrium was reached at a final pH of 4.21. The reaction solution was filtered, and the obtained product was dried at 90 °C for 2 hours.

It was then fired in a nitrogen ambience at 400 °C for 2 hours, thereby obtaining 7.5 g of a laminar powder (laminar powder C). This powder had a specific surface area of 270 m<sup>2</sup>/g, an aspect ratio of 50, and an average particle size of 20.0 μm. The pH of a 5 % aqueous suspension of this laminar powder as measured at 25 °C was 4.0.

#### Working Example 4

Laminar powder B obtained in Working Example 2 in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually added a solution that was prepared by dissolving 0.35 g of a natural colorant cochineal (carminic acid, a product of San'ei Chemical Co.) in 40 g water. The mixture was stirred

at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. After this colored powder was further subjected to a boiling process with 100 g of water, it was filtered, washed with water and then with ethanol, and dried at 80 °C, thereby obtaining a dark brown composite pigment (Invention Product 1) that had a vivid powder color.

Fig. 1 shows an SEM image of the obtained composite pigment. The pigment concentration was calculated based on the result of the carbon analysis conducted with a carbon analyzer Model EMIA-110, a product of Horiba Co., and the content of the pigment was found to be 14.8 %. The powder color of the pigment was measured by a colorimeter (Σ80, a product of Nippon Denshoku Co.). As a result, the hue (H) was found to be 3.55 R; the brightness (V), 2.64; and the chroma saturation (C), 10.05.

In addition, its extensibility (good spreadability, smoothness) on the surface of the skin, which is a required quality of a composite pigment as a cosmetic product, was examined by conducting an actual-use test (by 10 professional panelists), and it was found to be excellent.

#### Working Example 5

Laminar powder B [sic] obtained in Working Example 3 in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually added a solution that was prepared by dissolving 0.35 g of a natural colorant cochineal (carminic acid, a

product of San'ei Chemical Co.) in 40 g water. The mixture was stirred at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. After this colored powder was further subjected to a boiling process with 100 g of water, it was filtered, washed with water and then with ethanol, and dried at 80 °C, thereby obtaining a dark red composite pigment (Invention Product 2) that had a vivid powder color.

The obtained composite pigment contained the pigment in a quantity of 23.3 % and had  $H = 3.51$  R,  $V = 2.54$ , and  $C = 10.25$ .

In addition, its extensibility (good spreadability, smoothness) on the surface of the skin, which is a required quality of a composite pigment as a cosmetic product, was examined by conducting an actual-use test, and it was found to be excellent.

#### Working Example 6

Laminar powder B [sic] obtained in Working Example 3 in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually added a solution that was prepared by dissolving 0.15 g phloxin B [Red No. 104 (1), a product of Kishi Kasei Co.] in 40 g water. The mixture was stirred at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. This laminar powder was placed in an autoclave, and 100 g water was added, after which the suspension thus prepared was heated to 130 °C in 30 minutes, held at this temperature for 1 hour, and subsequently left to cool to 70 °C in 30 minutes. Next, it

was washed and dried, thereby obtaining a red composite pigment (Invention Product 3) having a vivid powder color.

The obtained composite pigment contained the pigment in a quantity of 10.5 % and had  $H = 5.18$  R,  $V = 3.80$ , and  $C = 14.30$ .

In addition, its extensibility (good spreadability, smoothness) on the surface of the skin, which is a required quality of a composite pigment as a cosmetic product, was examined by conducting an actual-use test, and it was found to be excellent.

#### Working Example 7

Laminar powder B [sic] obtained in Working Example 3 in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually added a solution that was prepared by dissolving 0.15 g tartrazine [Yellow No. 4, a product of Kishi Kasei Co.] in 40 g water. The mixture was stirred at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. This laminar powder was placed in an autoclave, and 100 g water was added, after which the suspension thus prepared was heated to 130 °C in 30 minutes, held at this temperature for 1 hour, and subsequently left to cool to 70 °C in 30 minutes. Next, it was washed and dried, thereby obtaining a yellow composite pigment (Invention Product 4) having a vivid powder color.

The obtained composite pigment contained the pigment in a quantity of 10.4 % and had  $H = 2.61$  Y,  $V = 6.46$ , and  $C = 14.50$ .

/131

In addition, its extensibility (good spreadability, smoothness) on the surface of the skin, which is a required quality of a composite pigment as a cosmetic product, was examined by conducting an actual-use test, and it was found to be excellent.

#### Working Example 8

Laminar powder B [sic] obtained in Working Example 3 in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually added a solution that was prepared by dissolving 0.15 g Brilliant Blue [Blue No. 1, a product of Kishi Kasei Co.] in 40 g water. The mixture was stirred at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. This laminar powder was placed in an autoclave, and 100 g water was added, after which the suspension thus prepared was heated to 130 °C in 30 minutes, held at this temperature for 1 hour, and subsequently left to cool to 70 °C in 30 minutes. Next, it was washed and dried, thereby obtaining a blue composite pigment (Invention Product 5) having a vivid powder color.

The obtained composite pigment contained the pigment in a quantity of 10.0 % and had  $H = 5.34$ ,  $B = 1.24$ , and  $C = 9.85$ .

In addition, its extensibility (good spreadability, smoothness) on the surface of the skin, which is a required quality of a composite pigment as a cosmetic product, was examined by conducting an actual-use test, and it was found to be excellent.

#### Comparative Example 1

To 200 g of ion-exchange water was added 10.0 g of the same laminar metallic aluminum obtained in Reference Example 1. The pH of the suspension at this stage as measured at 25 °C was 5.3. The suspension was stirred at 90 °C for 10 hours, but the reaction could not be fully completed, and the resulting product had a black ash color. The result of measuring its X-ray diffraction revealed that it was, in large part, still Al metal and only partially converted into an alumina hydrate.

#### Comparative Example 2

To 200 g of an aqueous solution of hydrochloric acid was added 10.0 g of the same laminar metallic aluminum obtained in Reference Example 1. The pH of the suspension at this stage as measured at 25 °C was 4.0. The suspension was stirred at 90 °C for 10 hours, but the reaction could not be fully completed, and the resulting product had a black ash color. The result of measuring its X-ray diffraction revealed that it was, in large part, still Al metal and only partially converted into an alumina hydrate.

#### Test Example 1

The water resistance and solvent resistance of Invention Products 1 through 5 obtained in Working Examples 4 through 8 were compared with those of commercially available products. More specifically, 0.2 g each of Invention Products 1 through 5 obtained in the aforesaid Working Examples and Comparative Example Products 1 through 3 shown

below was suspended in water, ethanol, or 0.3 % brine and shaken at 40 °C for 1 hour, after which it was filtered. The dye concentration in the filtrate was measured by spectrophotometric technique (with UV-200, a product of Shimazu Co.), thus finding the dissolved amount of the dye. The results are shown in Table 1 (the unit is ppb).

Comparative Example Product 1:

Lake pigment R104 (containing 19.4 % by weight of Red No. 104-1)

Comparative Example Product 2:

Lake pigment Y4 (containing 38.6 % by weight of Yellow No. 4)

Comparative Example Product 3:

Lake pigment B1 (containing 12.5 % of Blue No. 1)

TABLE 1

Test Samples	Water	Ethanol	0.3 % Brine
Invention Product 1	<10	<10	<10
Invention Product 2	<10	<10	<10
Invention Product 3	<10	<10	150
Invention Product 4	<10	<10	80
Invention Product 5	<10	<10	200
Comparative Example Product 1	1360	7000	2600
Comparative Example Product 2	923	1500	2800
Comparative Example Product 3	513	3600	800

As is evident from Table 1, the composite pigments of the present invention had excellent water resistance and solvent resistance.

Test Example 2

In order to quantify the extensibility (spreadability, smoothness) of a powder on the surface of the skin, the powder's coefficient of friction, which has high correlation with extensibility, was measured as an alternative characteristic. More specifically,



Invention Product 3 powder obtained in Working Example 6 was sandwiched between two aluminum discs, and, while a 100 g load was applied to one disc in the vertical direction, the other disc was rotated at 300 rpm, in which condition the torque was measured, /132 thereby finding the coefficient of friction of the powder. Mica (Comparative Example Product 5), which has good extensibility, was selected as a reference material, and the coefficient of friction of the powder was compared with that of mica. It was also compared with the coefficient of friction of an alumina pigment (Comparative Example Product 4) that was not laminar but granular. The results are shown in Table 2.

Comparative Example Product 4:

To 6.0 g of a commercially available active alumina (average particle size: 3.4  $\mu\text{m}$ , specific surface area: 270  $\text{m}^2/\text{g}$ , pore volume: 0.3  $\text{mL/g}$ ) was added 54.0 g water and stirred, to which suspension was added 32 mL of 0.1 N hydrochloric acid, and the mixture was stirred for 1 hour. An equilibrium was reached at a final pH of 4.66, as measured at 25 °C. The obtained product was filtered and dried at 90 °C for 2 hours.

Next, it was fired in a nitrogen ambience at 400 °C for 2 hours. The pH of a 5 % aqueous suspension of this powder was 4.6, as measured at 25 °C.

The aforesaid fired powder in a quantity of 1.0 g was suspended in 50 g water, to which suspension, while being stirred, was gradually

added a solution that was prepared by dissolving 0.15 g phloxin B [Red No. 104 (1), a product of Kishi Kasei Co.] in 40 g water. The mixture was stirred at 60 °C for 20 minutes and subsequently filtered and washed, thereby obtaining a colored laminar powder. This colored powder was further subjected to a boiling process with 100 g water. It was filtered, washed with water and then with ethanol, and dried at 80 °C, thereby obtaining a granular pigment having an average particle size of 4.5 µm.

#### Comparative Example Product 5

Commercially available mica (average particle size: 15.0 µm)

TABLE 2

Test Samples	Coefficient of Friction
Invention Product 3	0.49
Comparative Example Product 4	0.70
Comparative Example Product 5	0.47

As is evident from Table 2, the composite pigment of the present invention had a low coefficient of friction that was comparable to the coefficient of friction of mica.

#### 4. Brief Explanation of the Drawing

Fig. 1 is a photograph taken by an SEM, illustrating the particle structure of a composite pigment of the present invention.

FIG. 1



10 μm